



Paul E. Helliker  
Director

# Department of Pesticide Regulation



Gray Davis  
Governor

Winston H. Hickox  
Secretary, California  
Environmental  
Protection Agency

## MEMORANDUM

TO: John S. Sanders, Ph.D.  
Chief  
Environmental Monitoring and  
Pest Management Branch

FROM: DeeAn Jones, Environmental Research Scientist  
Pamela Wofford, Associate Environmental Research Scientist  
Kean S. Goh, Agricultural Program Supervisor IV  
Environmental Monitoring and  
Pest Management Branch

DATE: February 28, 2000

SUBJECT: RESULTS OF SURFACE WATER MONITORED FOR FORESTRY  
HERBICIDES IN THE YUOK ABORIGINAL TERRITORY OF THE  
KLAMATH RIVER WATERSHED, FALL 1999

### SCOPE OF THIS MEMORANDUM

The purpose of this memorandum is to provide results of water sampling conducted in the Klamath River watershed by the Department of Pesticide Regulation (DPR). This study was conducted in collaboration with the U.S. Environmental Protection Agency and the Yurok Tribe to address tribal concerns about the potential presence of herbicide residues in surface water. Tribal people live near land owned by a timber company that uses herbicides for forestry management. This memorandum summarizes the second sampling results of a three-year study, initiated in 1998 to monitor the occurrence of forestry herbicides, atrazine, triclopyr, and glyphosate, in selected creeks of the Klamath River watershed. Data included here are from September 13, 1999 to October 29, 1999, with results from chemical analyses. An in-depth interpretation of the data is not included here but will be provided in the final report, which will include data from all three years of the study.



On September 14, 16, and 20, 1999, samples were collected at three tributaries near the aerial application sites. These samples were collected on the actual date each application was made. Samples were taken at 8 time-intervals for sites E and F, and at 6-time intervals for site G (Table 1, Table 2, Figure 1). In addition, herbicide samples were collected from the batch mixture in the spray tank to be applied at each site.

On October 27, 1999, samples were collected at the same three sites mentioned above (Table 1, Table 2, Figure 1). Samples were taken after the water level had risen by the first rain-runoff. Samples were taken at 8 time-intervals for each site.

Table 1. Forest site and herbicide application descriptions in Del Norte County.

Site	Description	Application type	Application date	Application time	Acres treated	Total AI used (lb)	Application slope (%) <sup>a</sup>	Intermediate slope (%) <sup>b</sup>
E	Hoppaw Creek Tributary	Aerial	9/16/99	10:00	40	60 lb. triclopyr	47	none
F	Hunter Creek Tributary	Aerial	9/14/99	11:00	105	157.5 lb. triclopyr	52	7
G	Wilson Creek Tributary	Aerial	9/20/99	13:50	13	13 lb. glyphosate	27	26

a=change in elevation from top to bottom of application site (ft)/distance (ft) X 100

b=change in elevation from bottom of application to sampling site (ft)/distance (ft) X 100

Elevation and distance estimated on USGS 7.5 minute Quad maps

Table 2. Application and runoff site descriptions in Del Norte County.

Site	Description	Coordinates	Elevation	Distance from application site	Precipitation (inches) <sup>b</sup>
E	Hoppaw Creek Tributary	N 41° 32' 40.4", W 124° 00' 53.1" <sup>a</sup>	920 ft.	in application boundary	0.65
F	Hunter Creek Tributary	N 41° 35' 52.5", W 124° 01' 13.6"	120 ft.	1700 ft.	0.50
G	Wilson Creek Tributary	N 41° 37' 2.8", W 124° 05' 25.0"	40 ft.	1100 ft.	0.37

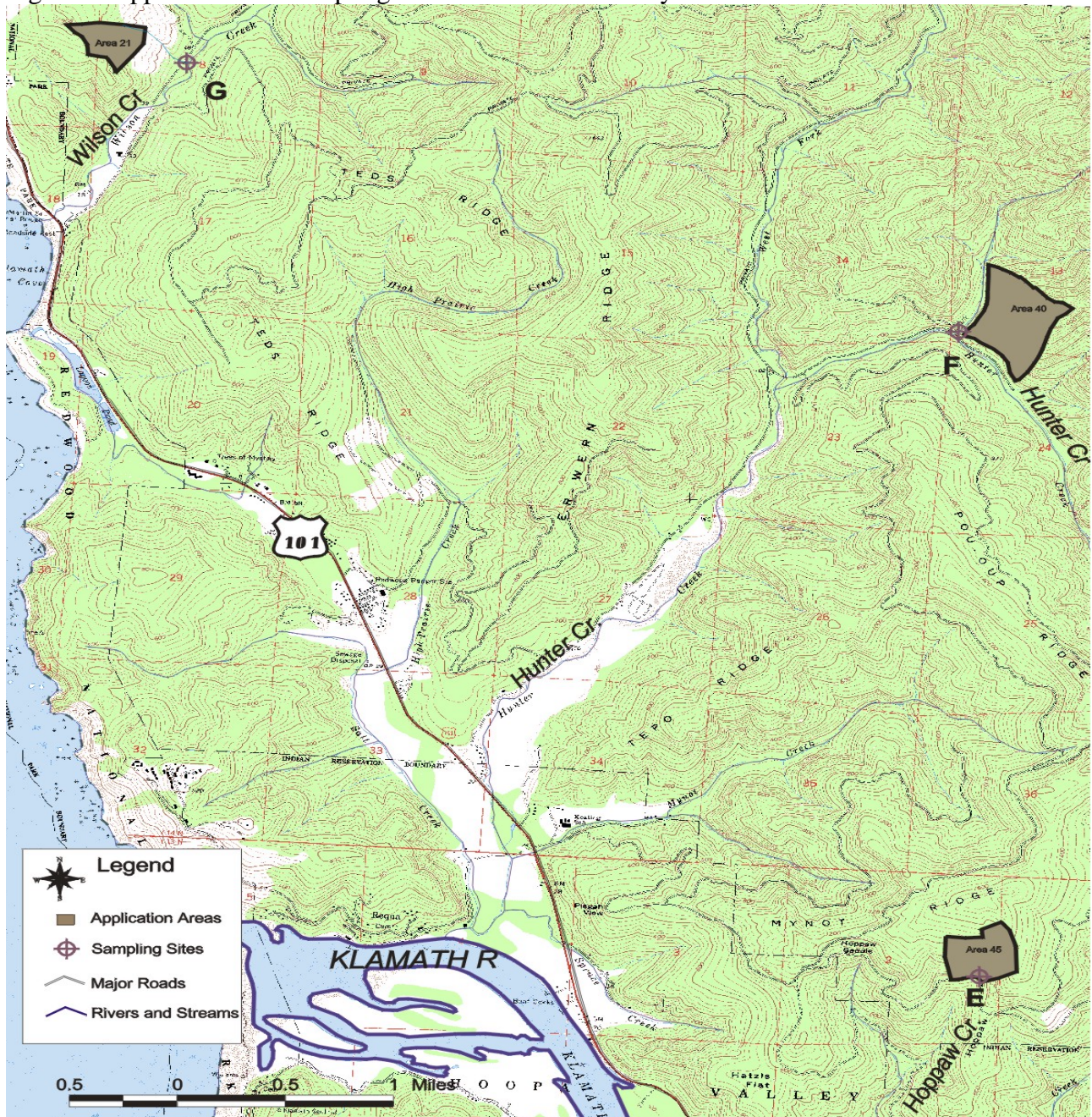
a=data at this site is uncorrected

b=precipitation collected in rain gauges from 10/26/99 at 18:00 to time sampler was started on 10/27/99 additional precipitation gauged at Terwer Creek station operated by DWR and USGS: 10/5/99, 21:00 to 10/6/99, 15:00= .56 in.; 10/26/99, 05:00 to 10/26/99, 11:00 = .44 in. Location= 41.5120° N, 123.999° W, Elevation 6 ft.



All water samples were collected as a grab sample from the main flow of the creek, using an ISCO automatic sampler. All samples were stored on wet ice or in a 4°C refrigerator until analysis.

Figure 1: Application and sampling sites in Del Norte County.



## **Environmental Measurements**

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using a Sentron® (model 1001) pH meter. Water temperature and EC were measured using an Orion® conductivity-salinity meter (model 140). DO was measured using an YSI® dissolved oxygen meter (model 58).

## **Herbicide Analyses**

Herbicide analyses of water samples were performed by the CDFA Center for Analytical Chemistry. Triclopyr, a phenoxy herbicide, was analyzed by gas chromatography (GC) on a capillary column using a mass selective detector (MSD). Glyphosate was analyzed by using high performance liquid chromatography (HPLC) with post-column derivatization and fluorescence detection. The reporting limit (reliable detection level) for triclopyr is 0.10 parts per billion (ppb), and 2.00 ppb for glyphosate.

## **RESULTS**

Tables 3 and 4 show chemical analysis results. Three tank samples were analyzed for the percentage of chemical mixed in each application batch. If mixed at the maximum allowable label rate for aerial applications, a tank mixture would contain: 2.2% of triclopyr or 20.75% glyphosate. The tank samples for sites E and F contained 1.07% and 1.45% triclopyr, respectively. The tank sample for site G contained 0.46% glyphosate. All applications were made within the label rates. There were no detections of any of the herbicides in the surface water samples during application. After the first rain event, there were also no detections of any of the herbicides in the runoff surface water samples from sites F and G. At site E, triclopyr was detected in all eight samples, ranging in concentration from 0.174 to 0.430 ppb ( $\mu\text{g/L}$ ).

All measured concentrations were below the North Coast Regional Water Quality Control Board's Water Quality Control Plan for the North Coast Region operational standard of 10 ppb. The measured concentrations of triclopyr were also below the California Department of Fish and Game (CDFG) estimated chronic toxicity threshold of 30  $\mu\text{g/L}$  (30 ppb) for triclopyr (DFG, 1994).

## **Environmental Measurements**

Table 5 presents the data for pH, DO, temperature, and EC. Water temperature ranged from 11.0 to 12.5°C, DO ranged from 9.15 to 10.84 mg/L, and EC values ranged from 49.4 to 109.0  $\mu\text{S/cm}$ . pH was recorded between 5.9 to 7.5. The California Regional Water Quality Control



Board (CRWQCB) (1994), lists the following water quality guidelines as acceptable for the Lower Klamath River hydrologic area (HA): DO above 8.0 mg/L, pH between 6.5 and 8.5, and EC below 200  $\mu$ S/cm 90% of the time (90% Upper Limit) and below 125  $\mu$ S/cm 50% of the time (50% Upper Limit). The plans do not provide an acceptable range for temperature, but the Lower Klamath River HA is designated as cold interstate water and its natural receiving water temperature shall not be altered. All DO, temperature, and EC measurements fall within CRWQCB's acceptable guidelines. The pH measurement taken at site G, on 9/20/99 was 5.9, and below the acceptable range. All other pH measurements fall within CRWQCB's acceptable guidelines.

Table 3. Concentrations of herbicides in spray tank and surface water samples taken during application.

Date	Time	Sample type	Site	Triclopyr	Glyphosate
9/16/99	9:30	Tank	E	1.07%	--
9/13/99	7:50	Tank	F	1.45%	--
9/20/99	9:00	Tank	G	-- <sup>a</sup>	0.46%
9/16/99	12:19	Water	E	ND <sup>b</sup>	--
	12:22	Water	E	ND	--
	12:25	Water	E	ND	--
	12:28	Water	E	ND	--
	12:38	Water	E	ND	--
	12:44	Water	E	ND	--
	12:51	Water	E	ND	--
	12:58	Water	E	ND	--
9/14/99	11:14	Water	F	ND	--
	11:19	Water	F	ND	--
	11:24	Water	F	ND	--
	11:29	Water	F	ND	--
	11:52	Water	F	ND	--
	12:07	Water	F	ND	--
	12:22	Water	F	ND	--
	12:35	Water	F	ND	--
9/20/99	13:55	Water	G	--	ND
	13:58	Water	G	--	ND
	14:01	Water	G	--	ND
	14:07	Water	G	--	ND
	14:12	Water	G	--	ND
	14:18	Water	G	--	ND

a=herbicide not used and hence not analyzed

b=ND - None detected at the reporting limit for that chemical.

Detection Level Reporting Limit: triclopyr = 0.1 ppb, glyphosate = 2.0 ppb

Table 4. Concentrations of herbicides in runoff surface water samples.

Date	Time	Sample type	Site	Triclopyr	Glyphosate
10/27/99	11:40	Water	E	0.255 ppb	-- <sup>a</sup>
	12:40	Water	E	0.174 ppb	--
	13:40	Water	E	0.251 ppb	--
	14:40	Water	E	0.430 ppb	--
	15:40	Water	E	0.389 ppb	--
	16:40	Water	E	0.243 ppb	--
	17:40	Water	E	0.219 ppb	--
	18:40	Water	E	0.204 ppb	--
10/27/99	10:06	Water	F	ND <sup>b</sup>	--
	11:06	Water	F	ND	--
	12:06	Water	F	ND	--
	13:06	Water	F	ND	--
	14:06	Water	F	ND	--
	15:06	Water	F	ND	--
	16:06	Water	F	ND	--
	17:06	Water	F	ND	--
10/27/99	9:19	Water	G	--	ND
	10:19	Water	G	--	ND
	11:19	Water	G	--	ND
	12:19	Water	G	--	ND
	13:19	Water	G	--	ND
	14:19	Water	G	--	ND
	15:19	Water	G	--	ND
	16:19	Water	G	--	ND

a=herbicide not used and hence not analyzed

b=ND - None detected at the reporting limit for that chemical.

Detection Level Reporting Limit: triclopyr = 0.1 ppb, glyphosate = 2.0 ppb

Table 5. Water quality measurement at sampling sites.

Date	Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)
9/16/99	E	11.7	*	9.15	49.4
9/14/99	F	12.5	7.2	9.30	77.0
9/20/99	G	12.2	5.9	9.77	96.0
10/28/99	E	11.0	7.5	10.12	60.0
10/28/99	F	11.4	7.5	10.32	81.0
10/28/99	G	11.0	7.0	10.84	109.0

\*unable to take reading- meter showed ERR (error)

## **References**

The California Regional Quality Control Board. 1994. Water Quality Control Plan, Region 1, North Coast Region. Santa Rosa, California.

The California Department of Water Resources, Division of Flood Management. California Data Exchange Center: October 1999. Internet address: [cdec.water.ca.gov/cgi-progs/queryF?s,station ID: tur](http://cdec.water.ca.gov/cgi-progs/queryF?s,station ID: tur).

California Department of Fish and Game. 1994. Preliminary hazard assessment of the herbicide triclopyr to fish and wildlife. Pesticide Investigations Unit. Environmental Services Division.